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Proton and Deuteron Magnetic Resonance Studies of Lamellar Lyotropic Mesophases†

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Abstract—Lyotropic liquid crystals of the lamellar type have been studied by means of deuteron and proton magnetic resonance. The deuteron resonance from D_2O molecules exhibit quadrupole splitting in the region of ~ 0 to 11 kHz. The origin of this splitting and its dependence on system composition and temperature has been investigated in both two- and three-component systems, containing different amphiphiles, such as *n*-octylamine, the corresponding hydrochloride and hydrobromide, nonylphenol polyethylene glycol ethers, *n*-octanoic acid and *n*-decanol. It has been shown that the quadrupole splitting can give information concerning the rate of deuteron exchange between water and amphiphilic molecules. Effects of solubilization of hydrocarbons on the quadrupole splitting have also been investigated. High resolution proton resonance signals have also been observed and the width and shape of these signals are discussed.

Some of the mesophases investigated can be aligned by means of a magnetic field of *ca.* 14 kilogauss. The alignment is displayed in both deuteron and proton resonance spectra.

1. Introduction

The application of NMR spectroscopy for the study of liquid crystals has been the subject of some recent review articles.(1–3) Relatively few of these papers have referred to lyotropic mesomorphic phases,(2,3) while the majority has concerned different types of thermotropic liquid crystals.(1) Since lyotropic mesophases have been shown to play an important role in biological systems,(4) we believe that a deeper understanding of their properties and structures could also illuminate some important biological problems, for example the

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† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

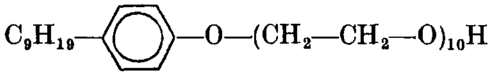
function of membranes. This work is mainly concerned with mesomorphic phases of the lamellar type with alternating layers of amphiphilic molecules and water. A large number of X-ray studies of such phases(5) indicates that in the amphiphilic layers the molecules are oriented parallel to each other with their long axis in a direction essentially perpendicular to the layer. With regard to the water layers, however, little is known about the structural changes originating from the interaction with the polar groups of the amphiphilic molecules. The main purpose of this investigation was to obtain further insight into the amphiphile-water interaction by means of proton and deuteron resonance measurements on various mesomorphic phases.

2. Experimental

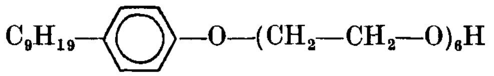
2.1. SAMPLE PREPARATION

Mesomorphic phases were prepared from mixtures of the following amphiphilic substances with deuterium oxide:

n-octylamine (OA), OAHCl, OAHBr, cetyltrimethylammonium bromide (CTAB), nonylphenol decaethylene glycol ether (NF-10), nonylphenol hexaethylene glycol ether (NF-6), *n*-octanoic acid and *n*-decanol.



NF-10



NF-6

In some cases hexadecane and *p*-xylene were solubilized in the phases. Purified samples of NF-10 and NF-6 were supplied by the Institute for Surface Chemistry in Stockholm. The numbers of polyethylene oxide units given in the above formulae are actually mean values of a distribution. The remaining chemicals were purchased from the British Drug Houses Ltd, Poole, England and from Fluka AG, Buchs, Switzerland, at the maximum purity available (always $\geqslant 99\%$). The D_2O used in the deuterated samples was obtained from Norsk Hydro, Norway and the enrichment amounted to 99.8%.

The samples were prepared by weight in glass ampoules or 5 mm

NMR tubes, which were immediately sealed off. The mixing was generally done by shaking at an elevated temperature, in most cases above the melting point of the mesomorphic phase. In some cases ultrasonic vibrations were applied to the samples in order to ensure homogeneity. The randomly oriented mesomorphic phases were prepared by decreasing the temperature of the corresponding isotropic solutions in the absence of the magnetic field, while the magnetically aligned phases were prepared by slowly decreasing the temperature of isotropic samples in the magnetic field (~ 14 kilogauss).

The phase diagrams of the binary and ternary systems studied in this investigation are given in the following references: OA—H_2O,(6) OAHCl—H_2O,(7) OA—OAHCl—H_2O,(8) OA—*n*-octanoic acid—H_2O,(8) OA—*p*-xylene—H_2O,(6) OAHCl—*n*-decanol—H_2O,(7) NF-10†—*p*-xylene—H_2O,(9) NF-10—*n*-hexadecane—H_2O,(9) NF-6†—*p*-xylene—H_2O,(9) CTAB—*n*-hexanol—H_2O.(10) The range of stability of the lamellar phase in the system OA—OAHBr—D_2O was estimated from the phase diagram of the system OA—OAHCl—H_2O.

2.2. NMR MEASUREMENTS

Wide-line NMR measurements were performed using a Varian V-4200 spectrometer equipped with a 12 inch V-3603 magnet. The magnetic field was regulated by a Varian Mark II Fieldial and the sample temperature was controlled by means of a Varian V-4540 Temperature Controller. At each temperature setting the actual temperature was measured using a copper-constantan thermocouple. The temperature was found to be accurate within ± 0.3 °C. Unless otherwise specified, all measurements were made at 20 °C. In order to facilitate a very slow temperature decrease (~0.1 °C/10 min), necessary for the preparation of oriented phases, a 10-turn 25Ω potentiometer was connected in series with the temperature setting resistor of the V-4540, and the external potentiometer was continuously varied by means of a motor with a low-geared transmission.

The frequency used in the wide-line measurements on deuterium was 9.1785 MHz. The variable frequency oscillator of the wide-line spectrometer was stabilized within ± 1 Hz by means of a crystal

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† The substances denoted by NF-6 and NF-10 in this paper are called EMU-02 and EMU-09, respectively, in Ref. (9).

oscillator. The power of the radio frequency field was always chosen so that no measurable saturation effect occurred. The magnetic field inhomogeneity, as measured on a D_2O sample, amounted to 20–30 milligauss. Most spectra were recorded using a 20 or 40 Hz modulation of the magnetic field and a small modulation amplitude compared with the linewidths. In spectra in which quadrupole coupling is observed, the linewidth can not be easily extracted from the spectrum, and in those cases the modulation amplitude was instead chosen so that no measurable change in line-shape resulted from a 50% increase in modulation amplitude.

The experimental parameter in the deuteron resonance spectra which is of primary interest is the frequency separation, $\Delta\nu$, between the absorption maxima in the powder patterns. The value of $\Delta\nu$ is approximately equal to the separation, $\Delta\nu'$, between the maximum and minimum in the derivative spectrum. However, when the line broadening superimposed on the powder pattern is not negligible compared with the quadrupole splitting, a correct evaluation of $\Delta\nu$ must take the complete lineshape of the powder pattern into consideration. This could be done by fitting a theoretical spectrum with a superimposed line broadening to the experimental spectrum. Instead of using this rather tedious procedure we have calculated a series of powder patterns assuming different linewidths, and in this way it has been possible to estimate the error resulting from the assumption that $\Delta\nu = \Delta\nu'$. The corrected value of $\Delta\nu$ can be approximately evaluated from the following expression

$$\Delta\nu = \Delta\nu' - (0.36 \pm 0.05)\,\delta \qquad (1)$$

where δ is the width at half maximum of the large peaks in the derivative spectrum. This expression is valid up to $\delta/\Delta\nu' \approx 0.5$. All experimental values have been corrected according to this procedure. The estimated error in the values of $\Delta\nu$ amounts to less than ± 5%.

High resolution experiments were performed using a Varian A-60A spectrometer equipped with a Varian V-6040 Temperature Controller. The r.f. field and sweep rate were always chosen to avoid distortion of the signals due to either fast sweep or saturation. The device for slow temperature decrease was also used for the high resolution experiments.

3. Deuterium Magnetic Resonance in Randomly Oriented Systems

3.1. THEORY

In the ^{2}H NMR spectra of the randomly oriented phases there were observed characteristic " powder " patterns arising from coupling of the deuterium quadrupole moment and the electric field gradients (EFG: s) at the nuclear position. Such patterns were first observed in other anisotropic mesomorphic phases by Lawson and Flautt(11,12) and later by Black, Lawson and Flautt,(13) Ellis, Lawrence, McDonald and Peel(14) and Charvolin and Rigny,(15) and they were, except in Ref. (14) explained as resulting from a partial orientation of the water molecules within randomly oriented aggregates in the sample. However, as pointed out by Ellis *et al.*,(14) when the amphiphilic molecules contain exchangeable protons, such as amines, carboxylic acids and alcohols, the quadrupole splitting may arise not only from partially oriented D_2O molecules, but also from deuterons covalently bound to partially oriented amphiphilic molecules. In the OA—D_2O system this mechanism of orientation of deuterium EFG:s has been found to be important. Different types of orientation mechanisms will be discussed in sec. 3.3.

It is of interest to note that rapid exchange of protons between partially oriented H_2O molecules will average out the dipole-dipole coupling while exchange of deuterons in partially oriented D_2O will not eliminate the quadrupole splitting (*cf.* Ref. (16)).

The interaction between a nuclear spin ($I = 1$) and an axially symmetrical EFG gives rise to a splitting of the resonance line into a doublet, with the frequency separation $\Delta\nu$ given by(17)

$$\Delta\nu = \left| \frac{3e^2qQ}{2h} \cdot \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle \right| \tag{2}$$

where q is the axial EFG, Q is the quadrupole moment of the nucleus ($I = 1$), θ is the angle between the applied magnetic field and the axis of the EFG, and the brackets denote time average.

In a polycrystalline sample all directions of the EFG relative to the magnetic field are equally probable and time independent. In such a case the $(3\cos^2\theta - 1)$ dependence of the quadrupole splitting gives rise to a powder pattern, in which the frequency separation between the two absorption maxima equals $3e^2qQ/4h$.(17)

In the case of a liquid crystal, however, the fact that θ is time dependent must be considered. A very useful formalism for the description of molecular orientation in liquid crystals has been developed by Saupe$^{(18)}$ and further treated by Buckingham and McLauchlan.$^{(19)}$ In the latter paper the authors have considered the case of partially oriented water molecules undergoing rapid reorientation. For a molecule with C_{2v} symmetry three elements of the orientation matrix are sufficient to describe the mean orientation, namely S_{11}, S_{22} and S_{33} in the nomenclature used in Ref. (19). However, all three are not necessary since only two are independent ($S_{11}+S_{22}+S_{33}=0$). The three molecule-fixed coordinate axes, 1, 2 and 3, have been chosen as depicted in Fig. 1. If the EFG is axially symmetric and its principal tensor component is directed along the O—D bond, the quadrupole splitting can be written as$^{(19)}$

$$\Delta\nu = \left| \frac{3}{2h} \cdot e^2qQ \left[S_{11}\left(\frac{3}{2}\cos^2\beta - \frac{1}{2}\right) + \frac{1}{2}(S_{22}-S_{33})\sin^2\beta \right] \cdot \left\langle \frac{3}{2}\cos^2\Omega - \frac{1}{2} \right\rangle \right| \tag{3}$$

where β is half the D—O—D angle of water (= 51° 16′), and Ω is the angle between the direction of the magnetic field and the constraint giving rise to the orientation.

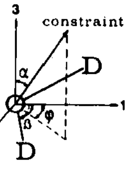

Figure 1. Choice of axes in the coordinate system fixed to the D_2O molecule.

Since a lamellar phase represents a uni-axial structure, the constraint set up by this structure is parallel to the direction perpendicular to the planes. In the phases investigated the experiments clearly show that once the lamellar phase has formed, the direction of the constraint is *unaffected* by the magnetic field, *i.e.* a powder pattern will not change to a measurable degree when the sample has been kept in the magnetic field for several days. (Still, most phases flow when the sample is tilted.)

In a randomly oriented phase a powder pattern is observed, with the frequency separation between the two absorption maxima being given by

$$\Delta\nu = \left| \frac{3e^2qQ}{4h} \cdot S \right| \tag{4}$$

where S is identical with the factor

$$\left[S_{11} \left(\frac{3}{2} \cos^2 \beta - \frac{1}{2} \right) + \frac{1}{2} (S_{22} - S_{33}) \sin^2 \beta \right]$$

characterizing the partial orientation of the water molecules with respect to the direction perpendicular to the water layers. Accurate experimental values of the quadrupole coupling constant, e^2qQ/h (in the following denoted by E_Q) and the asymmetry parameter, η, in D_2O are only known for the solid and gaseous states. The value of E_Q amounts to 215 kHz(20) (mean value) and 305 kHz(21,22) in the solid and gaseous states, respectively; the corresponding η values are 0.100(20) and 0.115,(21) respectively. It is reasonable to assume that, in the liquid state, both E_Q and η are intermediate between the values in solid and gaseous D_2O and closer to the values in the solid state.

The asymmetry of the EFG has not been considered in Eqs. (2)–(4). In fact, no theoretical treatment of the motional averaging of an asymmetric EFG has been reported in the literature. However, the observed spectra show a lineshape characteristic of a symmetric EFG, *i.e.* the separation between the outer shoulders of the absorption line is within experimental error exactly twice the separation between the maxima. It therefore appears that the average EFG is nearly symmetric and consequently Eq. (4) is applicable although the definition of S is only approximate. Changes in the observable quantity, $\Delta\nu$, can not be unambiguously related to a change in S unless the value of E_Q is constant. The value of E_Q may be influenced by variations in the degree of hydrogen bonding. The difference in the value of E_Q between solid and gaseous D_2O is not more than *ca.* 50%, and we therefore assume that the relatively small variations in the degree of hydrogen bonding present in the systems investigated do not markedly influence the value of E_Q.† However, since the value of E_Q is not known, we will in the following use the parameter $E_Q \cdot S$ for characterizing the partial orientation of D_2O.

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† This assumption is supported by deuteron relaxation investigations.(22a)

For deuterons bound to the amphiphilic groups the S parameter is defined as $\langle 3\cos^2\theta - 1\rangle$ (*cf.* Eqs. (2)–(4)) but in this case it is difficult to give an explicit expression for S in terms of orientation matrix elements. The parameter $E_Q \cdot S$ will also be used in this case to characterize the partial orientation.

The effect of chemical exchange on NMR lineshape in the presence of quadrupole coupling has not yet been given any detailed theoretical treatment. However, on the basis of the general principles of NMR it is possible to make some qualitative statements. Let us assume that deuterons are exchanging between chemically distinguishable sites, 1, 2, 3 . . . , which in the absence of exchange exhibit the quadrupole splittings $\Delta\nu_i$, $i = 1, 2, 3, \ldots$. If the lifetimes of the deuterons in the individual sites are much longer than the inverse of the differences in quadrupole splittings, *i.e.* $1/|(\Delta\nu_i - \Delta\nu_j)|$, separate resonance signals will be observed from the deuterons in the various sites. If, on the other hand, the lifetimes are much shorter than $1/|(\Delta\nu_i - \Delta\nu_j)|$, only an average resonance signal will be observed, for which the quadrupole splitting is given by

$$\Delta\nu = \sum_i x_i \Delta\nu_i \tag{5}$$

where x_i is the fraction of deuterons situated in site i. (Cf. also Ref. (14)). For the intermediate case, *i.e.* when the lifetimes and the values of $1/|(\Delta\nu_i - \Delta\nu_j)|$ are of the same order of magnitude, a more complicated lineshape may be expected.

3.2. RESULTS

In Fig. 2 the value of $E_Q \cdot S$ for D_2O is plotted *vs.* the mole fraction of D_2O in various types of lamellar mesomorphic phases at 20 °C. With the assumption that E_Q in D_2O equals 215 kHz, the S values of the partially oriented water molecules range between *ca.* 0.02 and ~ 0 in the phases investigated. From Fig. 2 it is apparent that an increasing mole fraction of D_2O, *i.e.* an increase in the thickness of the water layer, causes a reduction of $E_Q \cdot S$. This may indicate that a specific interaction occurs between the water molecules and the amphiphile. (The unusually large values of $E_Q \cdot S$ observed in the OA—D_2O system originate from a rapid exchange of water and amino deuterons, as will be discussed later.)

The temperature dependence of $E_Q \cdot S$ is illustrated in Fig. 3 for

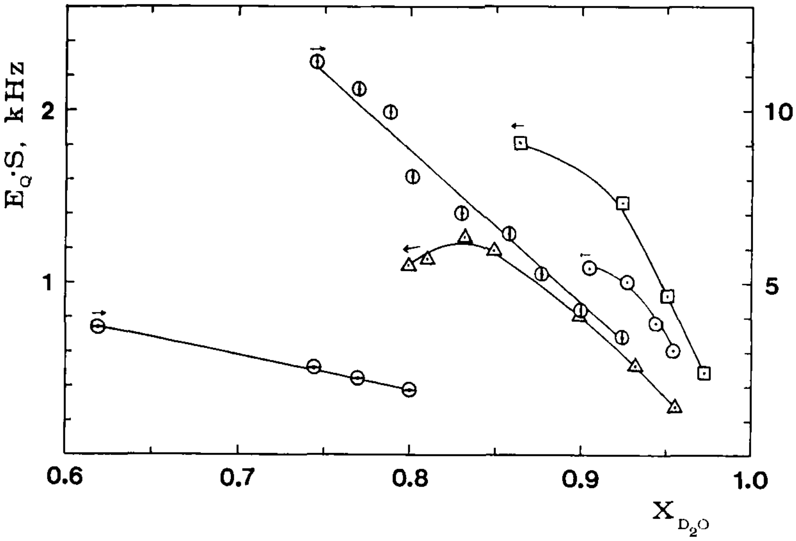

Figure 2. $E_Q \cdot S$ as a function of mole fraction of D_2O in different lamellar mesophases. Arrows indicate the proper ordinate scale.

Left ordinate scale:

⊡ NF-6
⊙ NF-10
◬ NF-10—*p*-xylene (mole ratio 1 : 2.5)

Right ordinate scale:

Φ OA
⊖ OAHCl

the different systems up to the melting point of the mesomorphic phases. The value of $E_Q \cdot S$ is usually lower at higher temperatures, probably due to a diminished degree of orientation of the D_2O and/or amphiphile molecules. (The increase in $E_Q \cdot S$ observed in the OAHCl—D_2O system is also accompanied by an increased line broadening and will be discussed later.) The relative decrease of the $E_Q \cdot S$ value at temperatures approaching the melting point varies considerably from system to system. Ellis *et al.*⁽¹⁴⁾ found in a lamellar phase of 1-mono-octanoin—D_2O that the value of $E_Q \cdot S$ showed no significant change in the temperature interval 15–40 °C.

The influence of the composition of the amphiphilic layer on the value of $E_Q \cdot S$ has been investigated in four ternary systems prepared by adding *n*-octanoic acid, OAHCl or OAHBr to the binary system OA—D_2O and by adding *n*-decanol to OAHCl—D_2O. In lameller

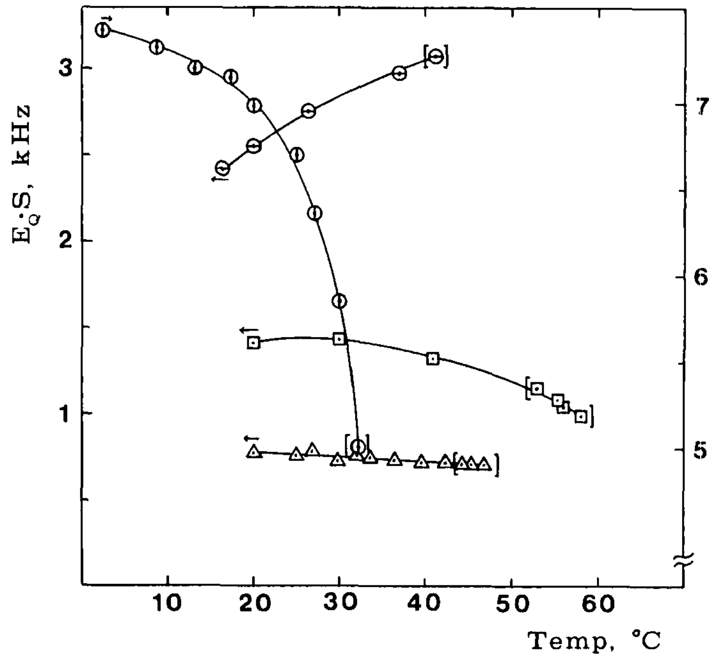

Figure 3. $E_Q \cdot S$ as a function of temperature. The parentheses indicate the presence of various amounts of isotropic phase and the arrows indicate the proper ordinate scale.

Left ordinate scale:

⊖ OAHCl—D_2O (mole ratio 1 : 2.90)
△ NF-10—D_2O (mole ratio 1 : 17)
⊡ NF-6—D_2O (mole ratio 1 : 12)

Right ordinate scale:

⦶ OA—D_2O (mole ratio 1 : 4.88)

phases with the mole fraction of D_2O constant at 0.770 the compositions of the amphiphilic layer was varied within the limits of stability of the various lamellar phases. In Fig. 4 $E_Q \cdot S$ is plotted *vs.* the molar ratio of acidic amphiphile to total amphiphile. The figure shows that an increase in the proportion of ionic amphiphile will generally lead to a reduction of $E_Q \cdot S$. Furthermore, there seems to be a counter-ion effect on the value of $E_Q \cdot S$, which may be seen from a comparison of OAHCl and OAHBr. In the system OAHCl—D_2O two different quadrupole splittings are observed. These have been assigned to ammonium and water deuterons which,

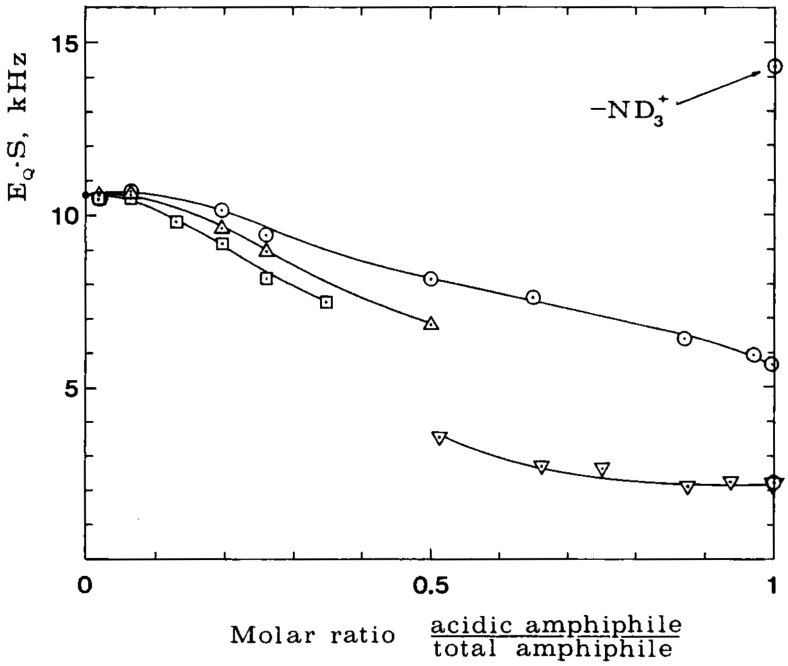

Figure 4. $E_Q \cdot S$ *vs.* the molar ratio of acidic amphiphile/total amphiphile at a constant mole fraction of D_2O equal to 0.770.

○ OA—OAHCl
△ OA—OAHBr
⊡ OA—*n*-octanoic acid
▽ *n*-decanol—OAHCl.

The point marked by ○, for which $E_Q \cdot S$ equals 5.7 kHz, corresponds to an abscissa value of 0.997.

due to slow deuteron exchange, give rise to separate resonance signals. In Figs. 2 and 3 the values of $E_Q \cdot S$ refer to the water deuterons.

In order to investigate the extent to which the S parameter is sensitive to solubilization, *p*-xylene was added to lamellar phases of NF-6—D_2O and NF-10—D_2O. To the latter system *n*-hexadecane was added in a separate experiment. The effect of the addition of non-amphiphilic compounds is shown in Fig. 5. On the addition of *n*-hexadecane to the NF-10—D_2O system $E_Q \cdot S$ is found to be approximately constant. Large amounts of *p*-xylene can be added

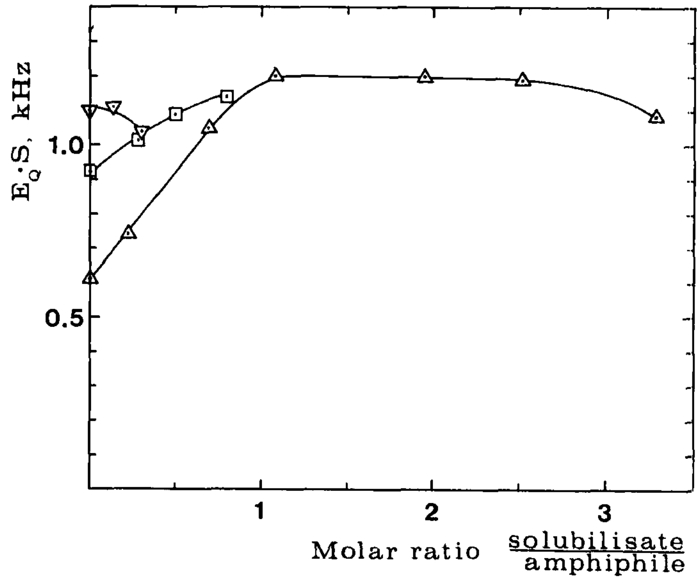

Figure 5. The influence of solubilization on the value of $E_Q \cdot S$ at constant molar ratio, x_{aw}, of amphiphile/water.

△ p-xylene in NF-10—D_2O, $x_{aw} = 1 : 21$
▽ n-hexadecane in NF-10—D_2O, $x_{aw} = 1 : 10$
⊡ p-xylene in NF-6—D_2O, $x_{aw} = 1 : 20$.

to the NF-6—D_2O and NF-10—D_2O systems, leading to a considerable increase in $E_Q \cdot S$. In the NF-10—D_2O system more than three p-xylene molecules can be solubilized per amphiphile molecule, but the value of $E_Q \cdot S$ only increases up to a concentration of *ca.* one p-xylene per amphiphile molecule.

3.3. DISCUSSION

(a) *General Considerations*

The quadrupole splittings observed in the deuteron magnetic resonance spectra of the mesomorphic systems investigated originate from an anisotropic orientation of the EFG : s felt by deuterons. This can arise either from partial orientation of D_2O molecules or from covalent binding of deuterons to the amphiphilic molecules in the lamellae. A partial orientation of water molecules may arise from their interaction with the hydrophilic groups of the amphiphile and it is possible to conceive of at least three different mechanisms of molecular interaction, which to some extent may give rise to a transfer of the partial orientation of the amphiphilic molecules to the water molecules: (i) hydrogen bonding, (ii) ion-dipole and/or dipole-dipole interaction, (iii) dispersion forces.

A change in the quadrupole splitting can arise both from a change in the amphiphile-water interaction and from an altered degree of partial orientation of the amphiphilic molecules. According to the commonly accepted picture of the organization of lamellar mesophases(5) the orientation of the amphiphilic molecules must be highly anisotropic, and thus the relative change in their degree of orientation is expected to be small. We therefore assume that the variations in S observed on changing the composition of the hydrophilic part of the system are to a large extent caused by a change in the water-amphiphile interaction, but it is not possible, from the experimental results in the present investigation, to separate the two effects.

A mechanism of interaction between water and amphiphile molecules likely to be of little importance is that due to anisotropic dispersion forces (iii) which would require a penetration of water molecules into the hydrocarbon region of the lamellae. It is true that in the case of polyethylene oxide surfactants penetration of water molecules to the ether oxygen groups will most probably occur, but then the interaction is likely to be dominated by the mechanisms involving hydrogen bonding (i) and/or dipole interaction (ii). Recent investigations of micellar systems(23) have led to the hypothesis that water molecules may penetrate to the hydrocarbon region of the micelles. If such a mechanism significantly contributed to the preferential orientation of water molecules in anisotropic mesophases, a measurable quadrupole splitting would also be observed in the absence of hydrogen bonding, as for example in the hexagonal phase of CTAB—D_2O. Preliminary investigations indicate, however, that $E_Q \cdot S$ in this system is very small. (See also Sect. 3(e).) The ion-dipole interaction can only contribute to the water orientation in the presence of ionic surfactants.

The result of the amphiphile-water interaction can be thought of as an orientation of the water molecules close to the hydrophilic groups, the remaining water molecules being less affected. This mechanism can only be consistent with the experimental results if rapid exchange is assumed between oriented and isotropic water, since in all systems investigated a simple powder pattern without any central peak is observed using deuterium magnetic resonance. (Cf. also Ref. (12)). The term " rapid exchange " used in the foregoing discussion means that the rate of exchange is much larger than the deuteron quadrupole interaction (of the order of 10^4 sec^{-1}). At rapid exchange of D_2O molecules between two sites, 1 and 2, corresponding to different quadrupole splittings, $\Delta\nu_1$ and $\Delta\nu_2$, the observed splitting, $\Delta\nu$, would be given by

$$\Delta\nu = x_1\Delta\nu_1 + x_2\Delta\nu_2 \tag{6}$$

where x_1 and x_2 are the fractions of D_2O molecules in the two sites (cf. Eq. (5)). Let us consider the model proposed by Lawson and Flautt(12) in which the two sites correspond to surfactant-associated water and self-associated water. If the self-associated water is considered to be essentially isotropic the corresponding term in Eq. (6) would vanish. If we assume that the number of water molecules bound to the hydrophilic groups is small compared with the number of isotropic water molecules and is directly proportional to the number of amphiphile molecules, Eq. (6) would lead to the following expression for the quadrupole splitting.

$$\Delta\nu = \text{const.}\ (1 - x_{D_2O})\Delta\nu_b \tag{7}$$

In this equation x_{D_2O} denotes the mole fraction of D_2O in the system and $\Delta\nu_b$ is the quadrupole splitting for the bound D_2O molecules. Therefore, under the further assumption that $\Delta\nu_b$ is independent of the composition of the system, the quadrupole splitting due to partial orientation of the water molecules would, at high water content, decrease approximately linearly at increasing mole fraction of D_2O.

(b) *Effects of Deuteron Exchange between Water and Amphiphile*

In most mesophases studied in this investigation the amphiphilic molecules contain exchangeable protons, such as amine, hydroxyl and carboxyl protons, and we have therefore also to consider the possible effects of deuteron exchange on the observed quadrupole splittings. The previously discussed two-site model has then to be modified to also include the chemically distinguishable deuteron sites on the amphiphilic molecules. However, since in all systems investigated the water deuterons only give rise to one average resonance signal, the discussion may be simplified by assuming only one water deuteron site corresponding to the average quadrupole splitting of the water deuterons. In the case of slow deuteron exchange between water and amphiphilic molecules, separate resonance signals may be observed for the different types of deuterons, which is found to be the case in the OAHCl—D_2O system (Fig. 4). If, on the other hand, the deuterons are rapidly exchanging between water and amphiphilic molecules, an average quadrupole splitting will be observed (*cf.* Eq. (5)), which is given by

$$\langle \Delta\nu \rangle = x_w \Delta\nu_w + \sum_i x_{ai} \Delta\nu_{ai} \tag{8}$$

where x_w is the mole fraction of water deuterons and x_{ai} is the mole fraction corresponding to the ith site of exchangeable amphiphilic deuterons. $\Delta\nu_w$ and $\Delta\nu_{ai}$ are the respective quadrupole splittings in the absence of exchange.

The fact that an average *proton* chemical shift is observed for water, amino and carboxyl protons in the mesomorphic phases investigated indicates that the rate of proton exchange is in these cases rapid enough to average out the chemical shift differences between the various types of protons. An important question for the interpretation of the quadrupole splitting data is whether this rate of exchange is sufficiently rapid to also average out the differences in quadrupole splitting. In the OAHCl—D_2O system separate powder patterns are observed at 20 °C for amino and water deuterons while only a very small addition of OA will change the spectrum into a single powder pattern, in which the splitting is consistent with Eq. 8. (See Fig. 4). These observations are in accordance with the known pH dependence of the amino proton exchange rate.(24) We therefore conclude that in the OA—OAHCl—D_2O system, the observed quadrupole splitting is a mean value of the splitting in the amino and water deuterons except at low pH. In the OAHCl—D_2O system an upper limit can be established for the rate of amino deuteron exchange at 20 °C. This is given by the difference in quadrupole splitting at slow exchange, $\sim 10^4$ sec^{-1}.

In the system OA—*n*-octanoic acid—D_2O the degree of protonation of the carboxylic groups is expected to be extremely small, and consequently the binding of deuterons to these groups will not measurably influence the value of $E_Q \cdot S$.

In the case of hydroxyl groups proton magnetic resonance measurements have shown that in the NF-6—H_2O system (mole ratio 1 : 1, corresponding to an isotropic phase⁽⁹⁾), the temperature has to be increased to *ca.* 70 °C before hydroxyl and water proton resonance lines coalesce. Therefore, at that temperature the rate of exchange is of the same order of magnitude as the chemical shift difference between water and hydroxyl protons (*ca.* 10 Hz). Consequently, the exchange rate at 20 °C will certainly be much too slow to average out the quadrupole coupling for hydroxyl and water deuterons, which is of the order of kHz. However, attempts to observe separate hydroxyl and water deuteron quadrupole splittings in the lamellar phase have failed, most probably due to the small mole fractions of hydroxyl deuterons. The effect of hydroxyl deuteron exchange on $E_Q \cdot S$ will be thoroughly discussed elsewhere.(25) Ellis *et al.*(14) have explained the quadrupole splitting observed in the lamellar phase of 1-mono-octanoin—D_2O as originating only from rapid exchange between hydroxyl and water deuterons. In view of the results of the present investigation we would suggest that the quadrupole splitting in this system can alternatively be explained as an effect of partial orientation of water molecules. (*Cf.* also Ref. (25).)

Our experimental results concerning the effects of deuteron exchange on the measured quadrupole splittings may be summarized in the following way. In the OA—D_2O system the average splitting between water and amine deuterons is observed even upon the addition of acidic amphiphile. Only at low pH are separate resonance signals obtained. For the amphiphiles containing hydroxyl groups the deuteron exchange has been found to be slow in the systems investigated. However, in this case, the separate hydroxyl deuteron resonance has not been observed, probably due to its low intensity.

(c) *Temperature Dependence of $E_Q \cdot S$*

The value of $E_Q \cdot S$ seems in most cases to decrease at higher temperature, probably due to a decrease in the degree of partial orientation of water molecules. The increase in $E_Q \cdot S$ (Fig. 3) and the increased line broadening at higher temperature observed in a lamellar phase of OAHCl—D_2O may tentatively be interpreted as due to chemical exchange phenomena.

No theoretical expressions are available for the complete description of the coalescence of two powder patterns arising from quadrupole interaction, with increasing rate of exchange. We assume, however, that the theoretical principles developed by Gutowsky, McCall and Slichter(26) for exchange effects on NMR lineshapes in the presence of chemical shifts and spin-spin couplings may also be valid in the case of quadrupole coupling, at least as long as the direction of the constraint is the same in the chemically distinguishable positions. In the lamellar phase of OAHCl—D_2O this direction is parallel to the optical axis for both N—D and O—D bonds. With increasing temperature the rate of exchange between ammonium and water deuterons is expected to increase and this may, according to the theory mentioned above,(26) result in an increase in the line broadening superimposed upon the theoretical powder patterns and also in an approach of the two powder patterns towards the powder pattern corresponding to rapid exchange. The latter effect may account for the increased splitting of the narrow powder pattern with increasing temperature (Fig. 3). This interpretation is supported by the preliminary observation that no increase in $E_Q \cdot S$ with increasing temperature is observed on rapid deuteron exchange produced by the addition of a small amount of OA to the system OAHCl—D_2O. Since the resonance corresponding to the ammonium deuterons is difficult to detect, its change with temperature has not yet been studied.

A similar increase in $E_Q \cdot S$ at increasing temperature has recently been reported in systems containing hydroxylic deuterons(25) and it has also been explained in terms of exchange phenomena.

(d) *Validity of Two-Site Model for Water Orientation*

The hypothetical mechanism for the partial orientation of the water molecules which was discussed above and which led to Eq. 7 may now be compared with the experimental results in Fig. 2. It should be pointed out that a linear decrease in $E_Q \cdot S$ with increasing mole fraction of D_2O similar to that proposed by Eq. (7) may also be inferred in the case of rapid exchange between amphiphile and water deuterons (*cf.* Ref. (14)), but a different slope is expected. Fig. 2 shows that, in the systems investgated, the hypothetical and oversimplified model can account for the approximately linear decrease in $E_Q \cdot S$ with increasing mole fraction of D_2O observed at high water content, but it is not in all cases capable of describing the detailed variation in $E_Q \cdot S$ at lower water content. Ellis *et al.*⁽¹⁴⁾ have found a linear decrease in the quadrupole splitting in accordance with Eq. (7) in a lamellar phase of 1-mono-octanoin—D_2O. In mesophases containing ionic amphiphiles marked deviations from such a linear dependence have been observed.⁽²⁵⁾

(e) *Interpretation of the S Parameter*

The definition of S as given in Eq. (4), though not exactly valid for an asymmetric EFG, may be used for a qualitative discussion of the dependence of S on the preferential orientation of D_2O molecules. As stated previously, two of the orientation matrix elements are mutually independent. Choosing for example S_{11} and S_{22} the S parameter may be written:

$$S = S_{11}\cos^2\beta + S_{22}\sin^2\beta = 0.375\,S_{11} + 0.625\,S_{22} \tag{9}$$

(assuming that $\beta = 52°\,16'$). According to Eq. (9) S equals zero either if $S_{11} = S_{22} = 0$, *i.e.* in an isotropic system, or if $S_{11} = -1.67\,S_{22}$. Variations in the S parameter may similarly be due either to changes in *degree* of orientation or changes in the *direction* of preferred orientation. The latter can be demonstrated using the models in Fig. 6. The S values were calculated according to Ref. (19), but they are not directly comparable with the experimental, firstly because exchange between bound and unbound water molecules must be considered and secondly since the motion of amphiphilic molecules will also influence the degree of orientation of the water molecules. The calculated S values should therefore be reduced by a factor which is assumed to be approximately equal in the three cases. Case *a* corresponds to hydrogen bonding between a deuteron in the D_2O molecule and a lone-pair orbital on the hydrophilic group, case *b* to hydrogen bonding between a lone-pair orbital on D_2O and protons on the hydrophilic groups, and case *c* corresponds to ion-dipole interaction. As can be seen from Fig. 6 cases *a* and *b* correspond to approximately the same absolute magnitude of S, while case *c* gives a very small value of S. Therefore, according to this simple model, when preferential orientation of water is produced by ion-dipole interaction a relatively small value of S may be expected. This may contribute to the decrease in $E_Q \cdot S$ generally observed with an

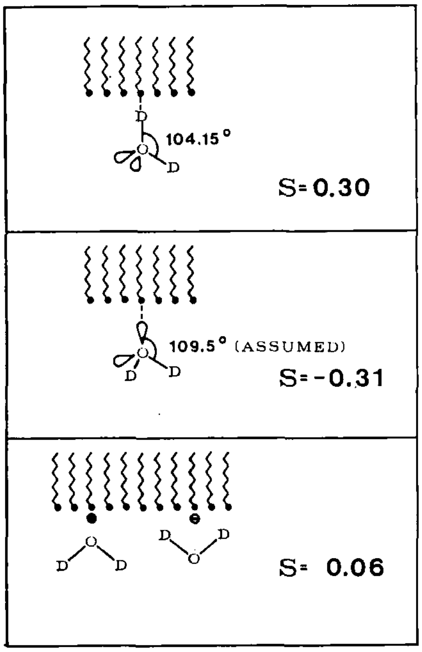

Figure 6. Theoretical values of the orientation parameter, S, for three different modes of orientation of the D_2O molecules.

increase in the proportion of ionic amphiphile in the lamellae (*cf.* Fig. 4). Furthermore, in the middle phase of CTAB—D_2O in which water molecules can not be hydrogen bonded to the hydrophilic groups, and consequently in which ion-dipole interaction may be the most important mechanism of orientation, a very small value of $E_Q \cdot S$ is observed (< 0.04 kHz).

We assume that an interpretation of variations in S in terms of the degree of orientation rather than the mode of orientation may be adequate only as long as the water bonding properties of the amphiphile are approximately constant. This is expected to be valid in most binary systems of amphiphile—water, but not in general in ternary systems.

(f) *Effects of Solubilization on* $E_Q \cdot S$

The solubilization of *p*-xylene in lamellar phases of NF-6—D_2O and NF-10—D_2O is found to markedly increase the value of $E_Q \cdot S$

(Fig. 5). In the latter system, in which up to three *p*-xylene molecules per NF-10 molecule can be solubilized, the value of $E_Q \cdot S$ only increases up to 1 molecule of solubilisate per amphiphilic molecule. This may suggest that the *p*-xylene molecules are located close to the hydrophilic groups at low concentrations, thereby increasing the degree of orientation of these groups. This could occur for example by means of a specific interaction between the aromatic rings in the *p*-xylene and NF-10 molecules. At higher concentrations of *p*-xylene the solubilization can be expected to result in an incorporation of *p*-xylene molecules in the aliphatic region of the lamellae, which would not primarily influence the degree of order of the hydrophilic groups. The solubilization of *n*-hexadecane in the system NF-10—D_2O does not markedly influence the value of $E_Q \cdot S$. These results from solubilization in lamellar mesophases may be compared with proton NMR investigations on solubilization in micellar systems(27) which indicate that aromatic hydrocarbons are in some cases located close to the polar groups of the amphiphile.

4. High Resolution PMR in Randomly Oriented Phases

The broadening mechanism of NMR absorption lines in liquid crystals was discussed by Weber(28) and later reviewed by Lawson and Flautt(2) for the case of amphiphilic systems. The dominating line broadening mechanism is considered to be the intramolecular magnetic dipole-dipole coupling,(28,2) which will not be averaged to zero in a system with anisotropic molecular motion. In a recent report on relaxation time measurements in amphiphilic mesomorphic phases Hansen and Lawson(29) suggested that molecular diffusion through magnetic inhomogeneities may also contribute to the linewidth. This has also been proposed by Penkett, Flook and Chapman(30) and by Kaufman, Steim and Gibbs.(31)

In the lamellar phase of NF-10—H_2O only two high resolution PMR signals are observed, one from the water protons (halfwidth *ca.* 10 Hz) and one from the polyethylene oxide chain protons (halfwidth *ca.* 30 Hz). The signals from the aromatic and aliphatic protons are strongly broadened as is the normal situation in such phases,(2) and are not observable. Preliminary measurements have shown that the linewidth of the polyethylene oxide protons is approximately independent of the magnitude of the magnetic field and we therefore conclude that the dipole-dipole coupling is the main broadening mechanism in this case. The relatively narrow linewidth indicates a rather high mobility of the polyethylene oxide chains which may result from a solvation effect of the water molecules. Another factor which may reduce the linewidth of the protons in these chains compared with ordinary aliphatic chains is the reduced intramolecular dipole-dipole coupling due to the ether oxygen bridges. The width of the water proton resonance signal in the NF-10—H_2O system increases somewhat with increasing magnetic field, but not in direct proportion to the magnetic field. From studies of the corresponding macroscopically oriented system (*cf.* Section 5) we conclude that the broadening of the water proton resonance line in this system may in part be due to dipole-dipole coupling in the partially oriented water molecules.

In the lamellar phases of OA—H_2O, OAHCl—H_2O, OA—OAHCl—H_2O and OA—n-octanoic acid—H_2O only the average resonance signal of water and amine protons is observable using high resolution techniques. In these systems a fine structure is observed in the resonance signal. This effect has been discussed in a previous paper,(32) where theoretical lineshapes were deduced under the assumption that the water protons experience different magnetic fields in the directions parallel and perpendicular to the lamellae. The agreement between experimental and calculated spectra is very good. The water proton resonance linewidths in these systems are considerably smaller than in the NF-10—H_2O system if the effect of susceptibility anisotropy is eliminated as described in Ref. (32). This may be due to a reduction of the dipole-dipole coupling by means of a higher water proton exchange rate in the amine–water system. The proton exchange in water is known to be both acid- and base-catalyzed.(33)

We intend to make a more detailed investigation of the proton resonance line broadening in these systems.

5. Magnetically Aligned Systems

The phases discussed in the preceding section can best be characterized as liquid crystalline "powders". Lawson and Flautt(11) and

Black *et al.*(13) demonstrated that lyotropic mesophases can be macroscopically oriented in magnetic fields, and they showed that such phases offered advantages compared with nematic phases as solvents in NMR studies of oriented molecules. As mentioned above the lamellar phases examined in this investigation do not spontaneously orient in the presence of a magnetic field of about 14 kilogauss. However, if the phases are heated above the melting point and then very slowly cooled (~0.1 °C/10 min.) in the magnetic field, some of the phases orient and maintain their orientation for at least 24 hours, even if the oriented sample is turned 90° from its original direction in the magnetic field. This persistent orientation is somewhat paradoxical since the macroscopic viscosity of the phases is not very high; they easily flow when the sample is tilted. The effect of magnetic orientation has been thoroughly studied in the NF-10—water system. The macroscopic orientation is displayed in both deuterium and proton resonance spectra.

In Fig. 7 high resolution proton magnetic resonance spectra recorded at various angles between the original orientation direction and the magnetic field are shown. At an angle of *ca.* 55° there is a minimum in the linewidth for the amphiphile protons, especially those of the polyethylene oxide chain. The most probable explanation for the observed angular variations in the linewidths is an incomplete averaging of the dipole-dipole coupling through molecular rotation. This process would necessarily result in a line broadening proportional to $(3 \cos^2 \Omega - 1)$, where Ω is the angle between the axis of rotation (roughly coinciding with the optical axis of the lamellar system) and the magnetic field direction.(34) This broadening vanishes at $\Omega \approx 55°$, leading to the linewidth minimum. A similar angular dependence of the proton resonance linewidth has previously been observed in an oriented lamellar mesophase.(35) The fact that the observed minimum in line broadening occurs when the oriented sample is turned an angle of ~55° from its original position in the magnetic field indicates that the molecular long axis is preferentially aligned parallel to the direction of the magnetic field during the slow cooling procedure. The residual linewidth at the observed minimum may have several explanations. A complete averaging through molecular rotation would imply perfect alignment, which can certainly not be expected. Another contribution to the linewidth can also

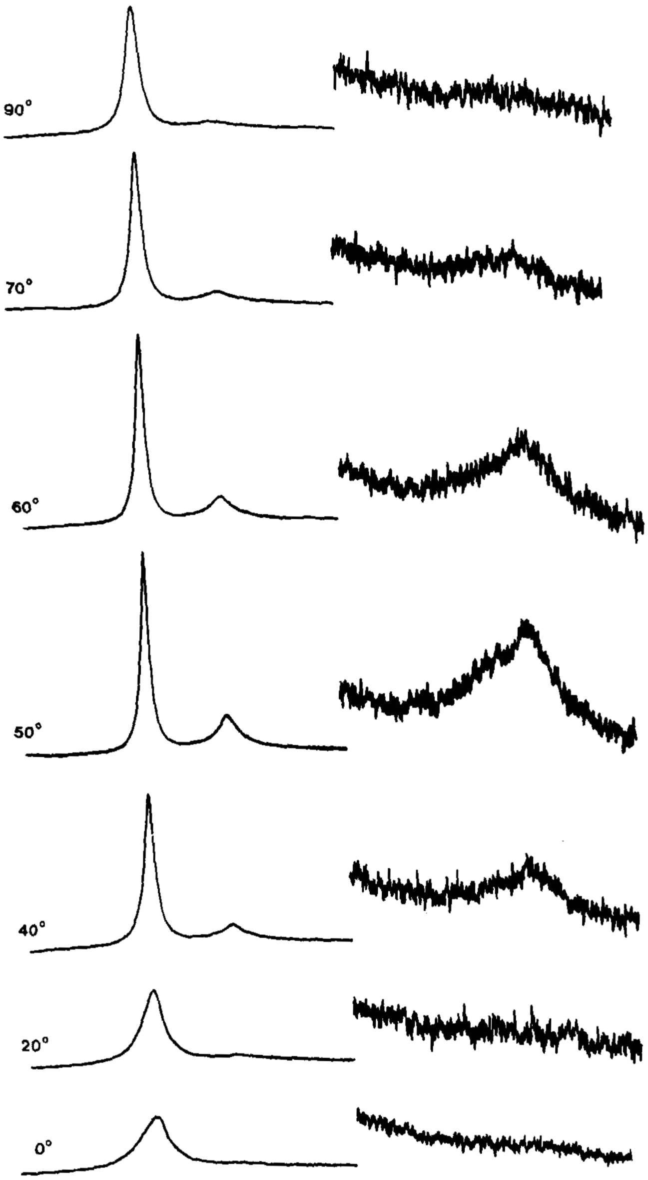

Figure 7. High resolution PMR spectra of an oriented lamellar mesophase of NF-10—H_2O, molar ratio 1 : 13, at different angles of rotation of the sample from its direction during the formation of the mesophase. From left to right the peaks correspond to the water protons, the polyethylene oxide chain protons and the aliphatic protons. For recording the right peak a tenfold amplification was used. Temperature: 45 ± 1 °C.

arise from magnetic inhomogeneities, as recently suggested by several authors.(29–31)

It may be seen from Fig. 7 that the linewidth of the water proton resonance is also angular dependent. This is interpreted as a residual dipole interaction arising from the anisotropic rotation of the water molecules. Proton exchange is assumed not to be sufficiently rapid to completely average out the dipole interaction. Buckingham and McLauchlan(19) have given the following expression for the dipole coupling, Δ^{HH}, in partially oriented water molecules

$$\Delta^{HH} = \frac{3}{2}\left|\left(\frac{3}{2}\cos^2\Omega - \frac{1}{2}\right) L^{HH}\cdot S_{22}\right| \tag{10}$$

where

$L^{HH} = \hbar(\gamma^H)^2/\pi(r^{HH})^3$

γ^H is the magnetogyric ratio for H,

r^{HH} is the interproton distance in water,

Ω is the angle between the constraint direction and the magnetic field, and

S_{22} has the same meaning as in Eq. (3).

Therefore, if the direction of the constraint coincides with the optical axis of the lamellae the linewidth of the water protons would also show the same type of angular dependence as that of the amphiphile protons. (See Fig. 7.)

The macroscopic orientation of the lamellar phase is also reflected in the quadrupole coupling observed in D_2O. This was for the first time observed by Lawson and Flautt.(11) Equation 3 shows that even the quadrupole coupling should be proportional to $(3\cos^2\Omega - 1)$, and this is in fact observed (Fig. 8). This angular dependence of the quadrupole coupling supports the conclusions from the proton resonance measurements, namely that the lamellar phase is aligned in the magnetic field with its optical axis parallel to the magnetic field direction. Therefore, sample spinning during the formation of the mesophase in the magnetic field will lead to a randomly oriented phase. The preferred direction of molecular orientation is consequently different from that in the lyotropic mesophase studied by Black *et al.*(13)

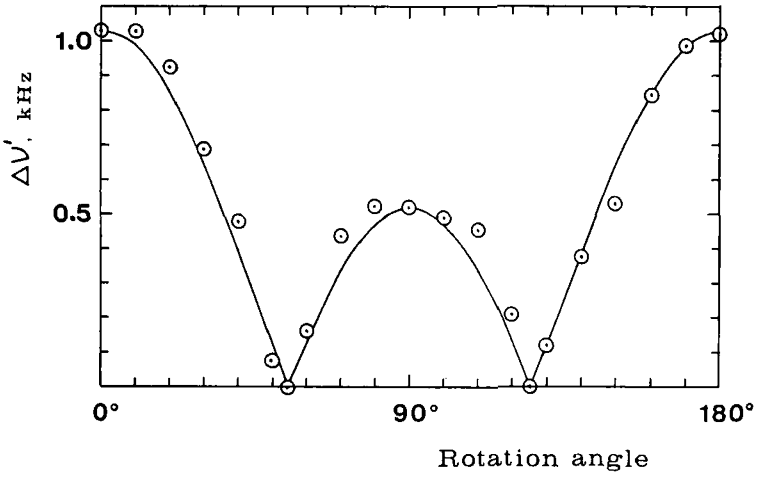

Figure 8. Frequency separation in the quadrupole doublet from oriented lamellar mesophase of NF-10—D_2O, mole ratio 1 : 17, as a function of the angle of sample rotation from the direction at the formation of the mesophase. (Temperature: 27 ± 1 °C.)

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